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A POSSIBLE COMMON INTERMEDIATE IN THE PHOTOCHEMICAL REACTIONS OF BENZENE

by

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SUMMARY

The benzene nucleus is known to undergo photochemical reactions of different types. In the present report it is suggested that all these reactions may involve one common highly reactive intermediate, different from the known excited singlet and triplet states. For this common intermediate a Möbius-type structure is proposed. The formation of valence tautomers is discussed employing elementary HMO.

Several - at first sight unrelated - photoreactions of the benzene nucleus have recently been discovered, viz.

1. Photoisomerizations, involving:

(a) translocations of substituents, e.g. isomerization of xylenes (1) and other di- and trialkylbenzenes (2, 3, 4);

(b) formation of non-aromatic isomers such as Dewar benzene (5, 6, 7), prismane (6, 7), benzvalene (6) and fulvene (8).

2. Photoreactions with various substrates at liquid nitrogen temperature (9-13b) or in viscous solvents (14).

In the course of our own research in this field it occurred to us that a common, highly reactive intermediate might be involved in all these photoreactions.

Van Tamelen's explanation of the stability of Dewar benzene (16) may give a clue as to the nature of this high-energy intermediate. According to his reasoning, Dewar benzene is stable, since <u>dis</u>rotatory ring opening of a cyclobutene ring in this compound would be unfavourable according to the Woodward-Hoffman rule (17), whereas <u>con</u>rotatory ring opening would lead to cis, cis, trans-cyclohexa-1, 3, 5-triene. A closer inspection of the latter structure reveals that it possesses the topology of a conjugated six-membered Möbius ring. Reversing Van Tamelen's argument, one concludes that collapse of a Möbius benzene ring to the Dewar structure in a <u>con</u>rotatory ring closure is energetically favourable. Dewar derivatives have in fact been isolated from irradiation products of tri- (6) and tetra(7)-tert-butylbenzene; and quite recently from hexafluorobenzene (18, 19).

Therefore we are inclined to assume a photochemical conversion of benzene into a Möbius structure, and subsequent <u>con</u>rotatory collapse of the latter to Dewar benzene and other valence tautomers. Other indications for a high-energy intermediate, different from electronically excited singlet and triplet states, have been previously discussed (20, 21) and the necessity of introducing such a species has even been stressed (12) — but only for special cases*.

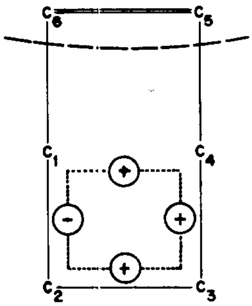
Möbius configurations of conjugated ring systems have been discussed from a theoretical viewpoint by Heilbronner (22) using HMO approximation, and more recently by Zimmerman (23, 23a). Since the Hückel method has been surprisingly successful in interpreting electrocyclic reactions (17, 24-27), it seemed of interest to use the same method in a discussion of the postulated Möbius intermediate and its transformations.

In HMO, benzene in its lowest excited state has a total π-electron energy of 6.00β. The Möbius isomer, which is described as a six-membered, conjugated ring with one exchange integral of opposite sign, has a ground-state π-electron energy of $4\sqrt{3}\beta'$** (ref. 22, 23, 23a). According to Heilbronner (22), for a Möbius ring consisting of n coplanar carbon atoms, $\beta' = \beta \cos \pi/n$; and therefore for six coplanar carbon atoms, $\beta' = \beta \cos 30^\circ$. Thus, the π-electron energy of Möbius benzene in units β becomes 6, and as fas as π-electron energy is involved, conversion of excited benzene to ground-state Möbius benzene may therefore be just possible. The formation of Dewar and valene structures from the hypothetical Möbius intermediate will now be considered.

A possible transition state for formation of Dewar benzene is pictured in (I); it consists of a localized double bond (C_5-C_6), and a conjugated four-membered ring ($C_1C_2C_3C_4$), the latter with exchange integrals β'', but with one (for the bond C_1-C_2) of opposite sign.

In HMO the π-electron energy of I becomes $2\beta + 5.656\,\beta''$ (for the isolated double bond, and the four-membered ring, respectively). Thus, if values of β' and β'' are not greatly different, the change in energy is favourable for the formation of Dewar from Möbius benzene.

Similarly, the formation of benzvalene may be envisaged (II); in this case the four-membered ring possesses a trans-annular bond as well. This is accomplished by the formation of two new bonds between C_1 and C_3, and between C_2 and C_4, as indicated.



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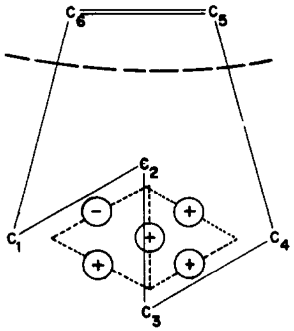

II

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* Cf. also the lecture by G. Porter at the Solvay Congress, Brussels 1965, and the subsequent discussion.

* * β', β'' etc. designate exchange integrals which presumably differ in value from that of benzene, β.

If an exchange integral of opposite sign is attributed to one of the outer bonds of the four-membered bridged ring (but not to the central bond) the π-electron energy becomes $2\beta + 6.000\beta'''$. The relatively large value of the coefficient of β'''may compensate for the possibly smaller absolute value of β''' compared to β'', and for the high σ-strain in benzvalene.

A benzvalene type isomer has been obtained by irradiation of 1, 2, 4-tri-tert-butylbenzene (6). It must, however, be admitted that benzene does not photochemically yield either benzvalene or the Dewar isomer. On the other hand, Dewar benzene could be prepared chemically and its half-life time at room temperature was estimated at about two days (15, 16). In contrast, the Dewar and benzvalene tautomers of tri-tert-butylbenzene appeared to be rather more stable (6). Thus, transient formation of such isomers from benzene during irradiation seems reasonable. Furthermore, photoisomerizations of xylenes (1) and other di- and tri-alkylbenzenes (2, 3, 4) strongly suggest Dewar, prismane or benzvalene derivatives to be involved.

The above discussion, which has only a tentative value, suggests a topological relationship between benzvalene, Dewar benzene and the Möbius structure. If we extend the term conrotation to include formation of benzvalene from Möbius benzene as indicated in II, then the three structures: benzvalene, Dewar and Möbius benzene are interconvertible by conrotatory processes. Structures which are related in this way will be called "topologically equivalent". This admittedly vague definition places Dewar benzene and benzvalene on the same footing, both being "topologically equivalent isomers" of Möbius benzene, whereas ground-state benzene, for example, is "topologically non-equivalent". These considerations make it possible to restate the present hypothesis: the photoreactions of benzene considered involve a common highly reactive intermediate. This intermediate, different from excited singlet and triplet benzene, is assumed to be topologically equivalent to a six-membered conjugated Möbius ring. Thus it may be invisaged either as a Möbius ring with coplanar ring atoms, or as one with a folded structure (cf. Heilbronner (22)), or as a folded ring with non-vanishing exchange integrals between several non-bonded ring atoms. Such interactions might to some extent compensate for the strain which such structures undoubtedly involve.

It seems necessary that in a Möbius structure the hybridization of the carbon atoms is different from sp_2. Catalin models are suitable to construct a model of Möbius benzene if one takes amino nitrogen (dihedrals 110°) instead of aromatic carbon (dihedrals 120°) for the ring atoms (Fig. 1). In this manner it is possible to construct a model in which the dihedrals formed by the ring bonds and neighbouring "C"-H bonds are of the order of magnitude of 30°. The p-orbitals then assume some lone-pair character; two are equatorial, the others pairwise alternatingly axial, whereas two hydrogen atoms are axially opposed, the others intermediate The ring is non-planar; it becomes rather a distorted chair-like configuration. Of course, this model is not intended to convey an exact representation of the Möbius-like intermediate; it may, however, be helpful in visualizing the topology.

Radiationless transition of the Möbius intermediate to the ground state of benzene, either directly or by way of intermediate compounds such as Dewar benzene or benzvalene, might constitute an alternative for fluorescence and inter-system cross-over (20) as suggested in ref. 20 and account for the "quantum deficit" (cf. note* on page 2 of the article).

Interpretation along similar lines of the second group of reactions, viz. photochemical reactions of benzene with various substrates, mostly at very low temperature (9-13b) or highly viscous solvent (14) will be the subject of a forthcoming publication.

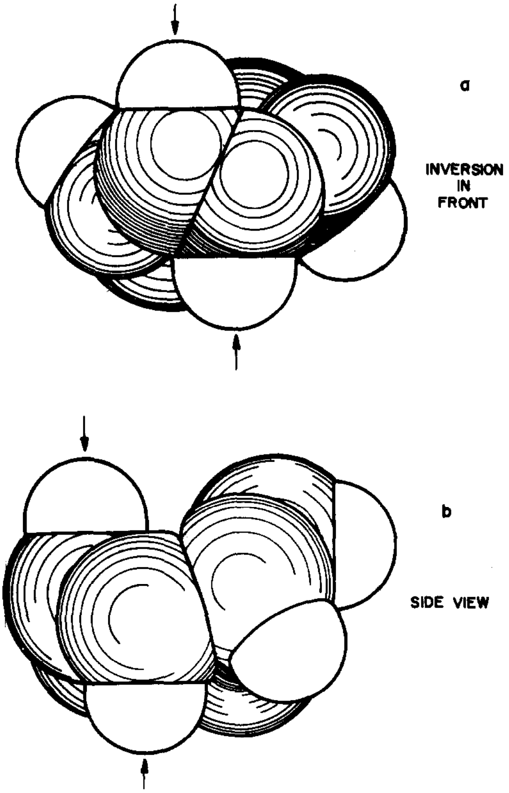

FIG. 1 Model of Möbius benzene

REFERENCES

1. K.E. Wiltzbach and L. Kaplan, J. Amer. Chem. Soc. 86 , 2307 (1964).
2. L. Kaplan, K.E. Wiltzbach, W.G. Brown and Shtl Shu Yang, J. Amer. Chem. Soc. 87, 675 (1965).
3. A.W. Burgstahler, Ping-LuChien and M.O. Abdel Rahman, J. Amer. Chem. Soc. 86, 5281 (1964).
4. A.W. Burgstahler and Ping-Lu Chien, J. Amer. Chem. Soc. 86, 2940 (1964).
5. E.E. van Tamelen and S.P. Pappas. J. Amer. Chem. Soc. 84, 3789 (1962).
6. K.E. Wiltzbach and L. Kaplan, J. Amer. Chem. Soc. 87, 4004 (1965).
7. E.M. Arnett and J.M. Bollinger, Tetrahedron Letters 1964, 3803.
8. H.J.F. Angus, J. McDonald Blair and D. Bryce-Smith, J. Chem. Soc. 1960, 2003.
9. B.N. Shelimov, N.V. Fok and V.V. Voevodskii: Doklady Akad. Nauk S.S.S.R. 144, 596 (1962).
10. V.C. Vinogradova, B.N. Shelimov. N.V. Fok and V.V. Voevodskii: Doklady Akad. Nauk S.S.S.R. 154, 188 (1963).
11. S.P. Odintsova, B.N. Shelimov, N.V. Fok and V.V. Voevodskii: Izvest. Akad. Nauk S.S.S.R., Ser. Khim. 1964, 572.
12. S. Leach, E. Migirdicyan and L. Graycar, J. chim. phys.. 56, 749 (1959).
13. E. Migirdicyan: J. chim. phys. 63, 520 (1966), 13a ibid. p. 535, 13b ibid. p. 543.
14. E.J. Anderton, H.T.J. Chilton and G. Porter, Proc. Chem. Soc. 1960, 352.
15. E.E. van Tamelen, Angew. Chem. 77, 759 (1965).
16. E.E. van Tamelen and S.P. Pappas, J. Amer. Chem. Soc. 85, 3297 (1963).
17. R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc. 87, 396 (1965).
18. G. Camaggi, F. Gozzo and G. Cevidalli, Chem. Comm. 1966, 313.
19. I. Haller, J. Amer. Chem. Soc. 88, 2070 (1966).
20. W.A. Noyes Jr., W.A. Mulac and D.A. Harter, J. Chem. Phys. 44, 2100 (1966).
21. A.K. Basak, G.P. Semeluk and I. Unger, J. Org. Chem. 70 1337 (1966).
22. E. Heilbronner, Tetrahedron Letters 1964, 1923.
23. H.E. Zimmerman, J. Amer. Chem. Soc. 88, 1564 (1966); 23a. ibid. p. 1566.
24. R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc. 87, 395 (1965).
25. R. Hoffmann and R.B. Woodward, J. Amer. Chem. Soc. 87, 2046 (1965).
26. R. Hoffmann and R.B. Woodward, J. Amer. Chem. Soc. 87, 4388-9 (1965).
27. R. Hoffmann and R.A. Olofson, J. Amer. Chem. Soc. 88, 943 (1966).